

Claims

- [c1] 1. A process and the products of the reaction, comprising reacting compounds referred to herein as Group 1 reagents, selected from a group of tetrachloroethylene, trichloroethylene, mixed tetrahaloethylenes, hexachlorocyclopentadiene and hexachlorobutadiene, with compounds referred to herein as Group 2 reagents, selected from a group of compounds, polymers and articles which have at least one methylene or methyne group which is adjacent to at least one electron withdrawing group selected from a group of ester, ether, carbonyl, nitrile, amide, nitro, sulfoxy, carbamyl, hydroxyl, or an aromatic ring groups, in the presence of free radicals, free radical initiators or their precursors, or when free radicals are created using ultrasound, UV light, ionizing radiation, and the like.
- [c2] 2. The method and the products of claim 1, wherein the Group 2 reagent is selected from a group of compounds, polymers and articles containing ethers and esters of alcohols containing methylene or methyne group adjacent to oxygen with carboxylic, inorganic, or polymeric acids; ketones, polyesters, polyester polyols, polyethers,

polyether polyols, and polyurethanes made with these polyols; poly-alkylacrylates, poly-alkylmethacrylates, poly-hydroxyalkylacrylates, poly-hydroxyalkylmethacrylates; polycarbonates made from aliphatic diols; alkyl carbonates, beta-ketoesters, beta-diketones, beta-dialkyl malonates, beta-diaryl malonates, cyclic esters and ethers, oxiranes, polylactones, ethylene-carbon monoxide copolymers; polymers and copolymers of polypropylene oxide and polyethylene oxide, polyvinyl acetate and its derivatives; ethylene-vinyl acetate copolymers, carbohydrates, polycarbohydrates, cellulose esters and ethers.

- [c3] 3. The method and the products of claim 1, wherein the Group 2 reagent is selected from a group of compounds, polymers and articles containing 1,4-dioxane, ethyl formate, propyl formate, butyl formate, isobutyl formate, amyl formate, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, secondary butyl acetate, amyl acetate, isoamyl acetate, methylisoamyl acetate, methoxybutyl acetate, 2-ethylbutyl acetate, hexyl acetate, cyclohexyl acetate, benzyl acetate, methyl propionate, ethyl propionate, butyl propionate, amyl propionate, methyl butyrate, ethyl butyrate, butyl butyrate, amyl butyrate, isoamyl butyrate, methyl acetoacetate, ethyl acetoac-

etate, ethyl acetone acetate, isoamyl isovelerate, methyl lactate, ethyl lactate, butyl lactate, amyl lactate, methyl benzoate, diethyl oxalate, ethylene glycol, ethylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol dimethyl ether, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, ethylene glycol monoethyl ether acetate, ethylene glycol isopropyl ether, ethylene glycol monobutyl ether, ethylene glycol monoisobutyl ether, ethylene glycol dibutyl ether, ethylene glycol monobutyl ether acetate, ethylene glycol isoamyl ether, ethylene glycol monohexyl ether, ethylene glycol monophenyl ether, ethylene glycol monophenyl ether acetate, ethylene glycol benzyl ether, methoxymethoxyethanol, ethylene glycol monoacetate, ethylene glycol diacetate, ethylene glycol butyric monoester, ethylene glycol propionic diester, ethylene glycol butyric diester, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monoisopropyl ether, diethylene glycol monobutyl ether, diethylene glycol monoisobutyl ether, diethylene glycol monobutyl ether acetate, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol methyl ethyl ether, diethylene glycol acetate, diethylene glycol dibutyl ether, propylene glycol, propylene glycol

monomethyl ether, propylene glycol monoethyl ether, propylene glycol monomethyl ether acetate, propylene glycol propyl ether, propylene glycol monoethyl ether acetate, propylene glycol monobutyl ether, dipropylene glycol, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol dimethyl ether, dipropylene glycol methyl ethyl ether, dipropylene glycol diethyl ether, trimethylene glycol, triethylene glycol dimethyl ether, butanediol, pentanediol, hexylene glycol, 3-methoxy-3-methoxybutanol, triethyl phosphate, .gamma.-butyrolactone, .gamma.-valerolactone, 6-hexanolactone, ethyl salicylate, butyl salicylate, diethyl adipate, ethyl carbonate, butyl sulfide, acetylacetone, ethyl acetate, ethyl propionate, ethyl butyrate, propyl acetate, iso-propyl acetate, n-butyl acetate, sec-butyl acetate, amyl acetate, benzyl acetate, hexyl acetate, heptyl acetate, octyl acetate, decyl acetate, dodecyl acetate, hexadecyl acetate, 1-methoxy-2-propanol acetate, butyl phthalate, benzyl acetate, furfuryl acetate, tetrahydrofurfuryl acetate, polyethylene terephthalate, epichlorohydrine, epoxy resins, gamma-butyrolactone, hydroxy-gamma-butyrolactone, acetoxy-gamma-butyrolactone, tetrahydrofurane, morpholine, N-methylmorpholine, N-methylmorpholine N-oxide, 4-alkylmorpholine, diethyl ether, isopropyl ether, dibutyl ether, diisoamyl ether, hexyl ether, ethyl phenyl ether, butyl phenyl ether,

ethyl benzyl ether, 2-methylfuran, tetrahydrofuran, tetrahydropyran, 2-ethoxytetrahydropyran, acetone, methyl ethyl ketone, cineole, acetone, methyl propyl ketone, methyl butyl ketone, methyl isobutyl ketone, methyl amyl ketone, methyl hexyl ketone, diethyl ketone, ethyl butyl ketone, dipropyl ketone, diisobutyl ketone, diacetone alcohol, phorone, isophorone, cyclohexanone, methylcyclohexanone, acetophenone, 1,3-diphenyl-2-propanone, benzoylacetone, nitrile, hydrocinnamone, nitrile, dibenzyl sulfoxide, ethylvinyl sulfone, dialkyl sulfone, alkylphenyl sulfone, acetonitrile, cyanoacetamide, and 1,3-cyclohexanedione, polyvinyl benzoate, polyvinyl propionate, polyvinyl butyrate, polyvinyl phthalate, fatty acid mono-, di-, and triglycerides, other glycerol esters and ethers, pentaerythritol esters and ethers, glucose, sucrose, sucrose esters, acetyl cellulose, alkyl, alkylhydroxyalkyl, hydroxyalkyl, and carboxyalkyl cellulose ethers, polybutene-1,4-diol, poly-beta-hydroxybutyrate, polylactide, polylactic acid, caprolactone, polycaprolactone.

[c4] 4. The method of claim 1, wherein the equivalent ratio between the Group 1 reagent and the active methylene groups in Group 2 reagent is between 1000:1 and 1:5.

[c5] 5. The method of claim 1, wherein the weight ratio between the free radical initiator and the Group 2 reagent

is between 1:1000 and 1:5.

- [c6] 6. The method of claim 1, wherein the reaction temperature is between 20 and 150°C.
- [c7] 7. The method of claim 1, wherein the reaction pressure is between 0.01 and 50 atmospheres.
- [c8] 8. The method of claim 1, wherein said reacting step is carried out for a time of about 1 to 50 hours.
- [c9] 9. The process including two vessels, Vessel 1 and Vessel 2, connected to allow the passage of vapors from Vessel 1 to Vessel 2 and the passage of liquids from Vessel 2 to Vessel 1, wherein the reagents are intermittently or continuously heated and distilled from the Vessel 1 and condensed into Vessel 2, then return as a liquid to the Vessel 1, wherein the catalysts, the reagents, or any combination of them are added to the Vessel 2 in a portion-wise or continuous way.
- [c10] 10. The process of claim 9, wherein the initial molar ratio of the Group 2 reagent to the Group 1 reagent (M_2/M_1) in the Vessel 1 is approximately the inverse of the ratio of the vapor pressures of the Group 2 reagent (VP_2) to the Group 1 reagent (VP_1), according to the formula: $M_2/M_1 = VP_1/VP_2$.

- [c11] 11. The process of claim 9, wherein the initial molar ratio of the Group 2 reagent to the Group 1 reagent (M2/M1) in the Vessel 2 is approximately 1:1.
- [c12] 12. The process of claim 9, wherein Vessel 2 contains the insoluble Group 2 reagent.
- [c13] 13. The process of claim 9, wherein Vessel 1 further contains free radical inhibitor or a mixture of inhibitors.
- [c14] 14. The process of claim 9, wherein Vessel 1 or the Vessel 2 further contains a base, or an inorganic peroxide, or an acid scavenger.
- [c15] 15. The process of claim 9, wherein the Vessel 1 or the Vessel 2 further contains a base selected from a group of alkali or alkali earth metal oxide, peroxide, hydroxide, carbonate, bicarbonate, aluminum hydroxide, or an organic or polymeric base or acid scavenger.
- [c16] 16. The method of claim 9, wherein the equivalent ratio between the Group 1 reagent and the active methylene groups in Group 2 reagent is between 1000:1 and 1:5.
- [c17] 17. The method of claim 9, wherein the weight ratio between the free radical initiator and the Group 2 reagent is between 1:1000 and 1:5.
- [c18] 18. The method of claim 9, wherein the reaction temper-

ature is between 20 and 150°C.

- [c19] 19. The method of claim 9, wherein the reaction pressure is between 0.01 and 50 atmospheres.
- [c20] 20. A method of claim 9, wherein the reagents and the catalyst are being added intermittently or continuously to the Vessel 2 and the reaction mixture is being removed intermittently or continuously from the Vessel 1.
- [c21]